

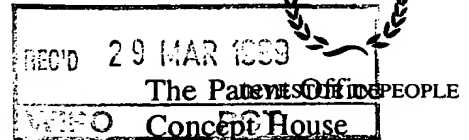


The  
Patent  
Office

PCT/GB 99/00292

12/8

09/601694



Cardiff Road  
Newport  
South Wales  
NP9 1RH

GB 99/00292

09/601694

09/6016945

I, the undersigned, being an officer duly authorised in accordance with Section 74(1) and (4) of the Deregulation & Contracting Out Act 1994, to sign and issue certificates on behalf of the Comptroller-General, hereby certify that annexed hereto is a true copy of the documents as originally filed in connection with the patent application identified therein.

In accordance with the Patents (Companies Re-registration) Rules 1982, if a company named in this certificate and any accompanying documents has re-registered under the Companies Act 1980 with the same name as that with which it was registered immediately before re-registration save for the substitution as, or inclusion as, the last part of the name of the words "public limited company" or their equivalents in Welsh, references to the name of the company in this certificate and any accompanying documents shall be treated as references to the name with which it is so re-registered.

In accordance with the rules, the words "public limited company" may be replaced by p.l.c., plc, P.L.C. or PLC.

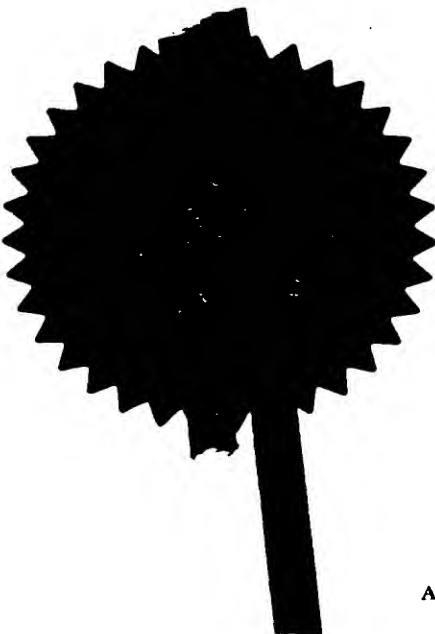
Re-registration under the Companies Act does not constitute a new legal entity but merely subjects the company to certain additional company law rules.

**PRIORITY  
DOCUMENT**  
SUBMITTED OR TRANSMITTED IN  
COMPLIANCE WITH RULE 17.1(a) OR (b)

Signed

Dated

1 MAR 1999



**THIS PAGE BLANK (USPTO)**

06-02-98 10:33  
06-FEB-1998 11:31

01734 242327  
FROM JOHNSON MATTHEY

P.04  
TO

R-298 JOB-001  
901633814444 P.04

Patents Form 1/77

Patent Act 1977  
(Rule 16)

The  
Patent  
Office

9802504.2

Request for grant of a patent

(See the notes on the back of this form. You can also get an explanatory leaflet from the Patent Office to help you fill in this form)

06 FEB 1998

06FEB98 E336158-1 D01091  
P01/7700 25.00 - 9802504.2  
The Patent Office

Cardiff Road  
Newport  
Gwent NP9 1RH

1. Your reference

AA 1389 GB

2. Patent application number

(The Patent Office will fill in this part)

3. Full name, address and postcode of the or of each applicant (underline all surnames)

JOHNSON MATTHEY PUBLIC LIMITED COMPANY  
2-4 COCKSPUR STREET  
TRAFALGAR SQUARE  
LONDON SW1Y 5BQ

Patents ADP number (if you know it)

If the applicant is a corporate body, give the country/state of its incorporation

GB

00536268007

4. Title of the invention

IMPROVEMENTS IN EMISSION CONTROL

5. Name of your agent (if you have one)

"Address for service" in the United Kingdom to which all correspondence should be sent (including the postcode)

IAN CARMICHAEL WISHART  
JOHNSON MATTHEY TECHNOLOGY CENTRE  
BLOUNTS COURT  
SONNING COMMON  
READING RG4 9NH

Patents ADP number (if you know it)

03991437001

6. If you are declaring priority from one or more earlier patent applications, give the country and the date of filing of the or of each of these earlier applications and (if you know it) the or each application number

Country

Priority application number  
(if you know it)

Date of filing  
(day / month / year)

7. If this application is divided or otherwise derived from an earlier UK application, give the number and the filing date of the earlier application

Number of earlier application

Date of filing  
(day / month / year)

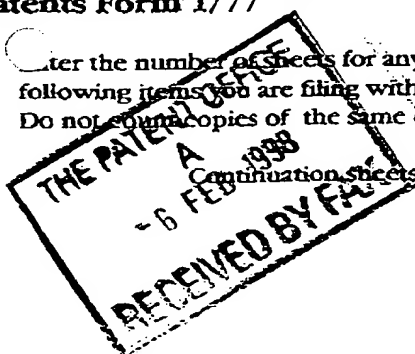
8. Is a statement of inventorship and of right to grant of a patent required in support of this request? (Answer 'Yes' if:

YES

- a) any applicant named in part 3 is not an inventor, or
  - b) there is an inventor who is not named as an applicant, or
  - c) any named applicant is a corporate body.
- See note (d))

## Patents Form 1/77

9. Enter the number of sheets for any of the following items you are filing with this form. Do not enter multiple copies of the same document.



Continuation sheets of this form

Description 6

Claim(s) 2

Abstract 1

Drawing(s) 4

10. If you are also filing any of the following, state how many against each item.

Priority documents

Translations of priority documents

Statement of inventorship and right to grant of a patent (Patents Form 7/77)

Request for preliminary examination and search (Patents Form 9/77)

ONE

Request for substantive examination (Patents Form 10/77)

Any other documents (please specify)

11.

I/We request the grant of a patent on the basis of this application.

Signature

Jewint

Date 6 Feb 98

I C WISHART

12. Name and daytime telephone number of person to contact in the United Kingdom

MRS F E STRANGE 0118 924 2125

## Warning

After an application for a patent has been filed, the Comptroller of the Patent Office will consider whether publication or communication of the invention should be prohibited or restricted under Section 22 of the Patents Act 1977. You will be informed if it is necessary to prohibit or restrict your invention in this way. Furthermore, if you live in the United Kingdom, Section 23 of the Patents Act 1977 stops you from applying for a patent abroad without first getting written permission from the Patent Office unless an application has been filed at least 6 weeks beforehand in the United Kingdom for a patent for the same invention and either no direction prohibiting publication or communication has been given, or any such direction has been revoked.

## Notes

- If you need help to fill in this form or you have any questions, please contact the Patent Office on 0645 500505.
- Write your answers in capital letters using black ink or you may type them.
- If there is not enough space for all the relevant details on any part of this form, please continue on a separate sheet of paper and write "see continuation sheet" in the relevant part(s). Any continuation sheet should be attached to this form.
- If you have answered 'Yes' Patents Form 7/77 will need to be filed.
- Once you have filled in the form you must remember to sign and date it.
- For details of the fee and ways to pay please contact the Patent Office.

AA 1389

1

IMPROVEMENTS IN EMISSION CONTROL

The present invention concerns improvements in emissions control, and especially concerns improvements in selective catalytic reduction of NO<sub>x</sub> in waste gas streams such as diesel engine exhausts or other lean exhaust gases such as from gasoline direct injection (GDI).

The technique named SCR (Selective Catalytic Reduction) is well established for industrial plant combustion gases, and may be broadly described as passing a hot exhaust gas over a catalyst in the presence of a nitrogenous reductant, especially ammonia or urea. This is effective to reduce the NO<sub>x</sub> content of the exhaust gases by about 20-25% at about 250°C, or possibly rather higher using a platinum catalyst, although platinum catalysts tend to oxidise NH<sub>3</sub> to NO<sub>x</sub> during higher temperature operation. We believe that SCR systems have been proposed for NO<sub>x</sub> reduction for vehicle engine exhausts, especially large or heavy duty diesel engines, but this does require on-board storage of such reductants, and is not believed to have met with commercial acceptability at this time.

We believe that if there could be a significant improvement in performance of SCR systems, they would find wider usage and may be introduced into vehicular applications. It is an aim of the present invention to improve significantly the conversion of NO<sub>x</sub> in a SCR system, and to improve the control of other pollutants using a SCR system.

Accordingly, the present invention provides an improved SCR catalyst system, comprising in combination an oxidation catalyst effective to convert NO to NO<sub>2</sub>, a source of reductant fluid and downstream of said source, an SCR catalyst. A preferred system incorporates a particulate filter interposed between the oxidation catalyst and the source of reductant fluid.

The invention further provides an improved method of reducing NO<sub>x</sub> in gas streams, comprising passing such gas stream over an oxidation catalyst under conditions effective to convert at least a portion of NO in the gas stream to NO<sub>2</sub>, adding reductant fluid to the gas stream containing enhanced NO<sub>2</sub> to form a gas mixture, and passing the gas mixture over

preferably, particulates are filtered out of the gas stream, desirably by a particulate filter between the oxidation catalyst and the source of reductant

The invention is believed to have particular application to the exhausts from heavy duty diesel engines, especially vehicle engines, eg truck or bus engines, but is not to be regarded as being limited thereto. Other applications might be LDD (light duty diesel), GDI, CNG (compressed natural gas) engines, ships or stationary sources. For simplicity, however, the majority of this description concerns such vehicle engines.

We have surprisingly found that a "pre-oxidising" step, which is not generally considered necessary because of the low content of CO and unburnt fuel in diesel exhausts, is particularly effective in increasing the conversion of NO<sub>x</sub> to N<sub>2</sub> by the SCR system. Desirably, the NO<sub>2</sub>/NO ratio is adjusted according to the present invention to the most beneficial such ratio for the particular SCR catalyst and CO and hydrocarbons are oxidized prior to the SCR catalyst. Thus, our preliminary results indicate that for a transition metal/zeolite catalyst it is desirable to convert all NO to NO<sub>2</sub>, whereas for a rare earth-based catalyst, a high ratio is desirable providing there is some NO, and for other transition metal-based catalysts gas mixtures are notably better than either substantially only NO or NO<sub>2</sub>. Even more surprisingly, the incorporation of a particulate filter permits still higher conversions of NO<sub>x</sub>.

The oxidation catalyst may be any suitable catalyst, and is generally available to those skilled in art. For example, a Pt catalyst deposited upon a ceramic or metal through-flow honeycomb support is particularly suitable. Suitable catalysts are e.g. Pt/Al<sub>2</sub>O<sub>3</sub> catalysts, containing 1-150g Pt/ft<sup>3</sup> (0.035-5.3g Pt/litre) catalyst volume depending on the NO<sub>2</sub>/NO ratio required.

The source of reductant fluid conveniently uses existing technology to inject fluid into the gas stream. For example, in the tests for the present invention, a mass controller was used to control supply of compressed NH<sub>3</sub>, which was injected through an annular

3

injector ring mounted in the exhaust pipe. The injector ring had a plurality of injection ports arranged around its periphery. A conventional diesel fuel injection system including pump and injector nozzle has been used to inject urea by the present applicants. A stream of compressed air was also injected around the nozzle; this provided good mixing and cooling.

5

The reductant fluid is suitably  $\text{NH}_3$ , but other reductant fluids including urea, ammonium carbamate and hydrocarbons including diesel fuel may also be considered. Diesel fuel is, of course, carried on board a diesel-powered vehicle, but diesel fuel itself is a less selective reductant than  $\text{NH}_3$  and is presently not preferred.

10

Suitable SCR catalysts are available in the art. A preferred catalyst at present is a  $\text{V}_2\text{O}_5/\text{WO}_3/\text{TiO}_2$  catalyst, supported on a honeycomb support. Although such a catalyst has shown good performance in the tests described hereafter and is commercially available, we have found that sustained high temperature operation can cause catalyst deactivation. Heavy duty diesel engines, which are almost exclusively turbocharged, can produce exhaust gases at greater than  $500^\circ\text{C}$  under conditions of high load and/or high speed, and such temperatures are sufficient to cause catalyst deactivation. In one embodiment of the invention, therefore, cooling means is provided upstream of the SCR catalyst. Cooling means may suitably be activated by sensing high catalyst temperatures or by other, less direct, means, such as determining conditions likely to lead to high catalyst temperatures. Suitable cooling means include water injection upstream of the SCR catalyst, or air injection, for example utilising the engine turbocharger to provide a stream of fresh intake air by-passing the engine. We have observed a loss of activity of the catalyst, however, using water injection, and air injection by modifying the turbocharger leads to higher space velocity over the catalyst which tends to reduce  $\text{NO}_x$  conversion. Preferably, the preferred SCR catalyst is maintained at a temperature from  $160^\circ\text{C}$  to  $450^\circ\text{C}$ .

We believe that in its presently preferred embodiments, the present invention may depend upon an incomplete conversion of  $\text{NO}$  to  $\text{NO}_2$ . Desirably, therefore, the oxidation catalyst, or the oxidation catalyst together with the particulate trap if used, yields a gas stream entering the SCR catalyst having a ratio of  $\text{NO}$  to  $\text{NO}_2$  of from about 4:1 to about 1:3

by vol, for the commercial vanadia-type catalyst. As mentioned above, other SCR catalysts perform better with different NO/NO<sub>2</sub> ratios. We do not believe that it has previously been suggested to adjust the NO/NO<sub>2</sub> ratio in order to improve NO<sub>x</sub> reduction.

5 A preferred embodiment of the present invention incorporates a particulate trap downstream of the oxidation catalyst. We discovered that soot-type particulates may be removed from a particulate trap by "combustion" in the presence of NO<sub>2</sub>. In effect, the incorporation of such a particulate trap serves to clean the exhaust gas of particulates without causing accumulation, with resultant blockage or back-pressure problems, whilst  
10 simultaneously reducing a proportion of the NO<sub>x</sub>. Suitable particulate traps are generally available, and are desirably of the type known as wall-flow filters.

A particularly interesting possibility arising from the present invention has especial application to light duty diesel engines (car and utility vehicles) and permits a significant  
15 reduction in volume and weight of the exhaust gas after-treatment system.

Several tests have been carried out in making the present invention. These are described below as examples of the invention, and are supported by results shown in graphical form in the attached drawings.

20

A commercial 10 litre turbocharged heavy duty diesel engine on a test-bed was used for all the tests described herein.

#### Test 1 - Comparative

25

A conventional SCR system using a commercial V<sub>2</sub>O<sub>5</sub>/WO<sub>3</sub>/TiO<sub>2</sub> catalyst, was adapted and fitted to the exhaust system of the engine. NH<sub>3</sub> was injected upstream of the SCR catalyst at varying ratios. The NH<sub>3</sub> was supplied from a cylinder of compressed gas and a conventional mass flow controller used to control the flow of NH<sub>3</sub> gas to an  
30 experimental injection ring. The injection ring was a 10cm diameter annular ring provided with 20 small injection ports arranged to inject gas in the direction of the exhaust gas flow.



5

NOx conversions were determined by fitting a NOx analyser before and after the SCR catalyst and are plotted against exhaust gas temperature in Figure 1. Temperatures were altered by maintaining the engine speed constant and altering the torque applied. It can readily be seen that at low temperatures, corresponding to light load, conversions are about 25%, and the highest conversions require stoichiometric (100%) addition of NH<sub>3</sub> at catalyst temperatures of from 325 to 400°C, and reach about 90%. However, we have determined that at greater than about 70% of stoichiometric NH<sub>3</sub> injection, NH<sub>3</sub> slips through the SCR catalyst unreacted, and can cause further pollution problems.

10 Test 2

The test rig was modified by inserting into the exhaust pipe upstream of the NH<sub>3</sub> injection, a commercial platinum oxidation catalyst of 10.5 inch diameter and 6 inch length (26.67cm diameter and 15.24cm length) containing 10g Pt/ft<sup>3</sup> (= 0.35g/litre) of catalyst volume. Identical tests were run, and it was observed from the results plotted in Figure 2, that even at 225°C, the conversion of NOx has increased from 25% to >60%. The greatest conversions were in excess of 95%. No slippage of NH<sub>3</sub> was observed in this test nor in the following test.

20 Test 3

The test rig was modified further, by inserting a particulate trap before the NH<sub>3</sub> injection point, and the tests run again under the same conditions. The results are plotted and shown in Figure 3. Surprisingly, there is a dramatic improvement in NOx conversion, and shown in Figure 3. Surprisingly, there is a dramatic improvement in NOx conversion, to above 90% at 225°C, and reaching 100% at 350°C. Additionally, of course, the particulates which are the most visible pollutant from diesel engines, are also controlled.

06-02-98 10:33  
06-FEB-1998 11:35

01734 242327  
FROM JOHNSON MATTHEY

P.12  
TO

R-298 Job-667  
901633814444 P.12

6

#### **Test 4**

An R49 test with 80% NH3 injection was carried out over a V2O5/WO3/TiO2 SCR catalyst. This gave 67% particulate, 89% HC and 87% NOx conversion; the results plotted in Figure 4.

5

CLAIMS

1. An improved SCR system for treating combustion exhaust gas containing NO<sub>x</sub>, comprising in combination an oxidation catalyst effective to convert at least a portion of NO in said NO<sub>x</sub> to NO<sub>2</sub>, a source of reductant fluid and an SCR catalyst.
2. An SCR system according to claim 1, wherein the reductant fluid is NH<sub>3</sub>.
3. An SCR system according to claim 1 or 2, wherein the oxidation catalyst is a platinum catalyst carried on a through-flow honeycomb support.
4. An SCR system according to claim 1, 2 or 3, comprising further a particulate filter interposed between the oxidation catalyst and the source of reductant fluid.
5. An SCR system according to claim 4, wherein said particulate filter is a wall-flow filter.
6. A diesel engine provided with an SCR system according to any one of claims 1 to 5.
7. A light duty diesel engine according to claim 6, wherein the volume of the exhaust gas after-treatment system is reduced.
8. A method of reducing NO<sub>x</sub> in gas streams, comprising passing such gas stream over an oxidation catalyst under conditions effective to convert at least a portion of NO in the gas stream to NO<sub>2</sub>, adding reductant fluid to the gas stream containing enhanced NO<sub>2</sub> to form a gas mixture, and passing the gas mixture over an SCR catalyst under NO<sub>x</sub> reduction conditions.
9. A method according to claim 8, wherein said gas stream is the exhaust from a diesel, GDI or CNG engine.

10. A method according to claim 8 or 9, comprising the additional step of filtering particulates from a diesel exhaust gas stream downstream of the oxidation catalyst.

5 11. A method of improving the conversion of NO<sub>x</sub> in exhaust gas streams using an SCR catalyst and a reductant, comprising adjusting the NO to NO<sub>2</sub> ratio to a level pre-determined to be optimum for said catalyst, by passing said exhaust gas through an oxidation catalyst.

06-02-98 10:33  
06-FEB-1998 11:36

01734 242327  
FROM JOHNSON MATTHEY

P.15  
TO

R-298 Job-551  
901633814444 P.15

9

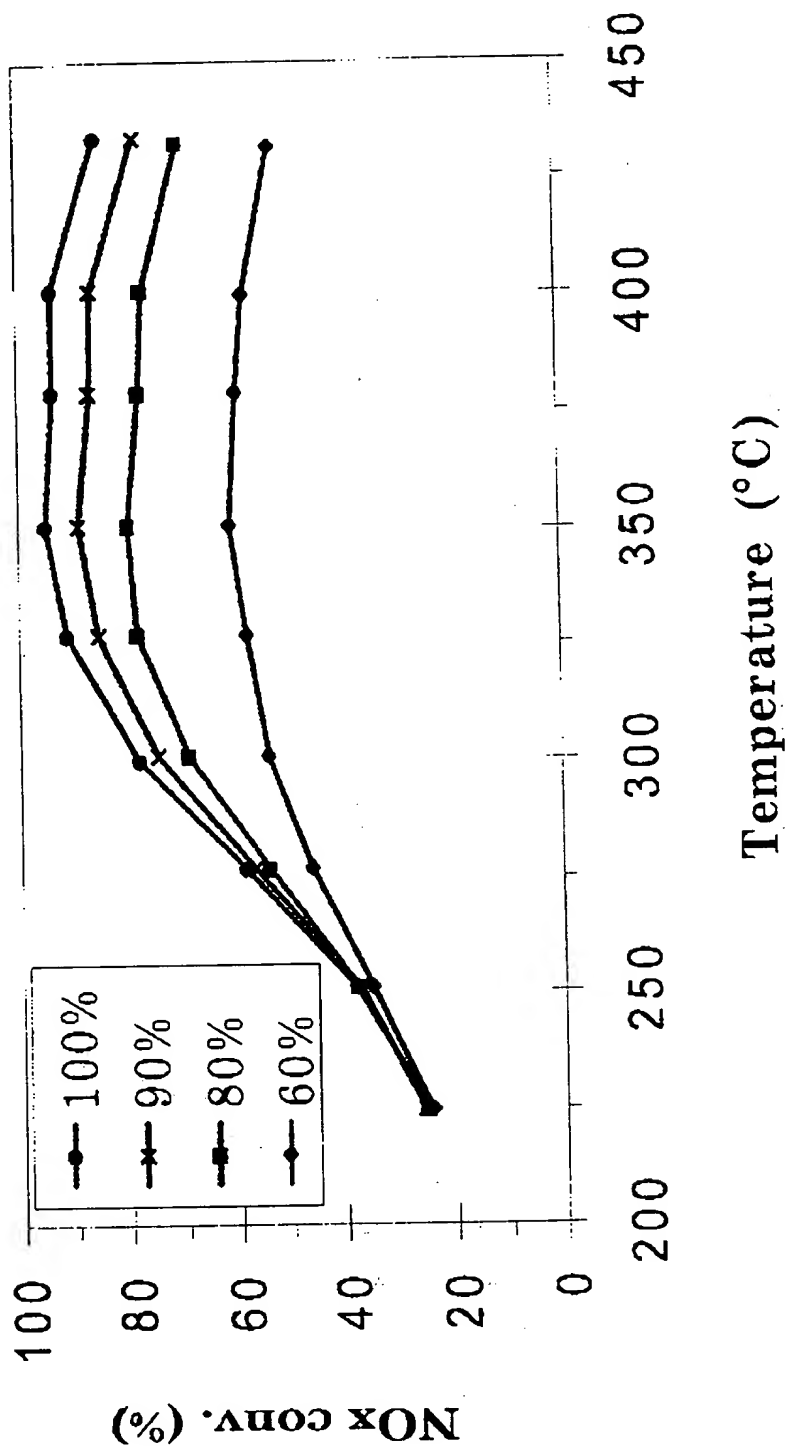
## IMPROVEMENTS IN EMISSION CONTROL

### Abstract of the Invention

- 5 A system for NOx reduction in combustion gases, especially from diesel engines, incorporates an oxidation catalyst to convert at least a portion of NO to NO<sub>2</sub>, a source of reductant such as NH<sub>3</sub>, and an SCR catalyst. A preferred system uses a particulate filter before the SCR catalyst. Considerable improvements in NOx conversion are observed.

**THIS PAGE BLANK (USPTO)**

**NO<sub>x</sub> Conversion vs T for different amounts of NH<sub>3</sub> Injection**  
NH<sub>3</sub> addition calculated at 1:1 NH<sub>3</sub>/NO and 4:3 NH<sub>3</sub>/NO<sub>2</sub>  
and 60-100% Injection of the calculated amount of NH<sub>3</sub>.

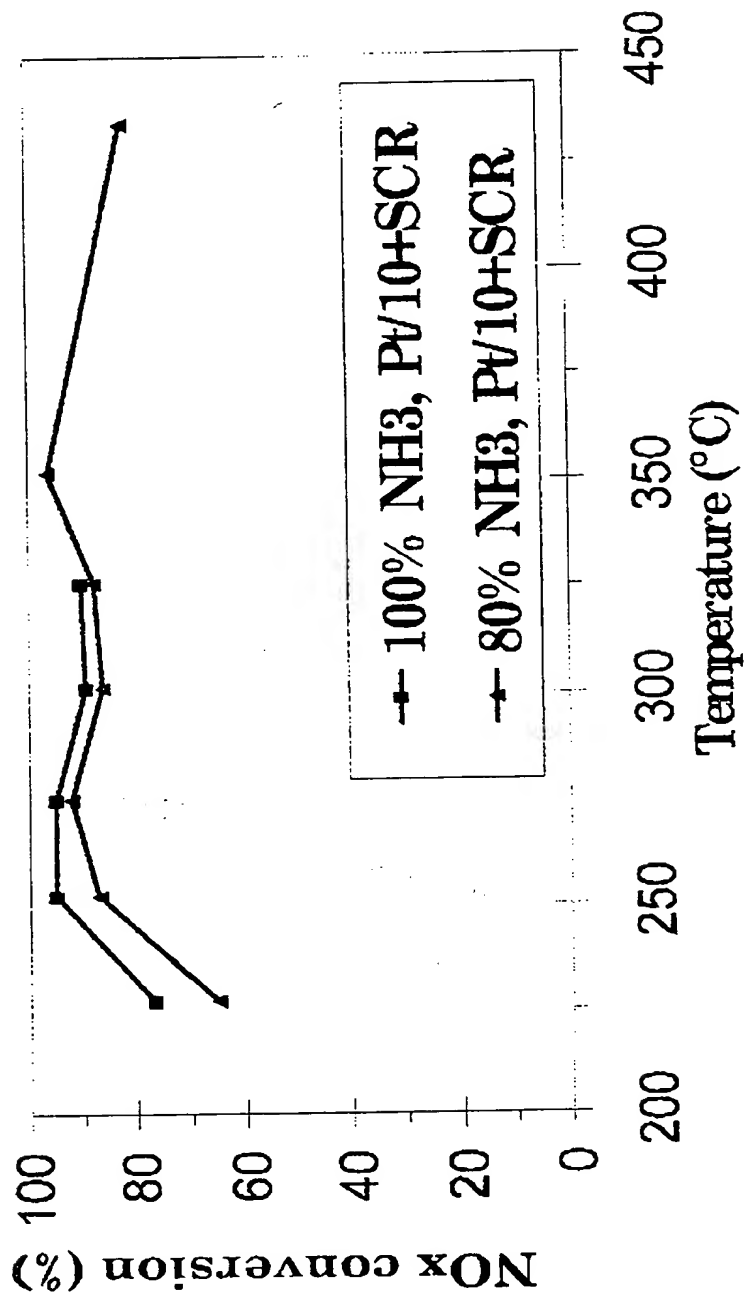


**THIS PAGE BLANK (USPTO)**



2/4

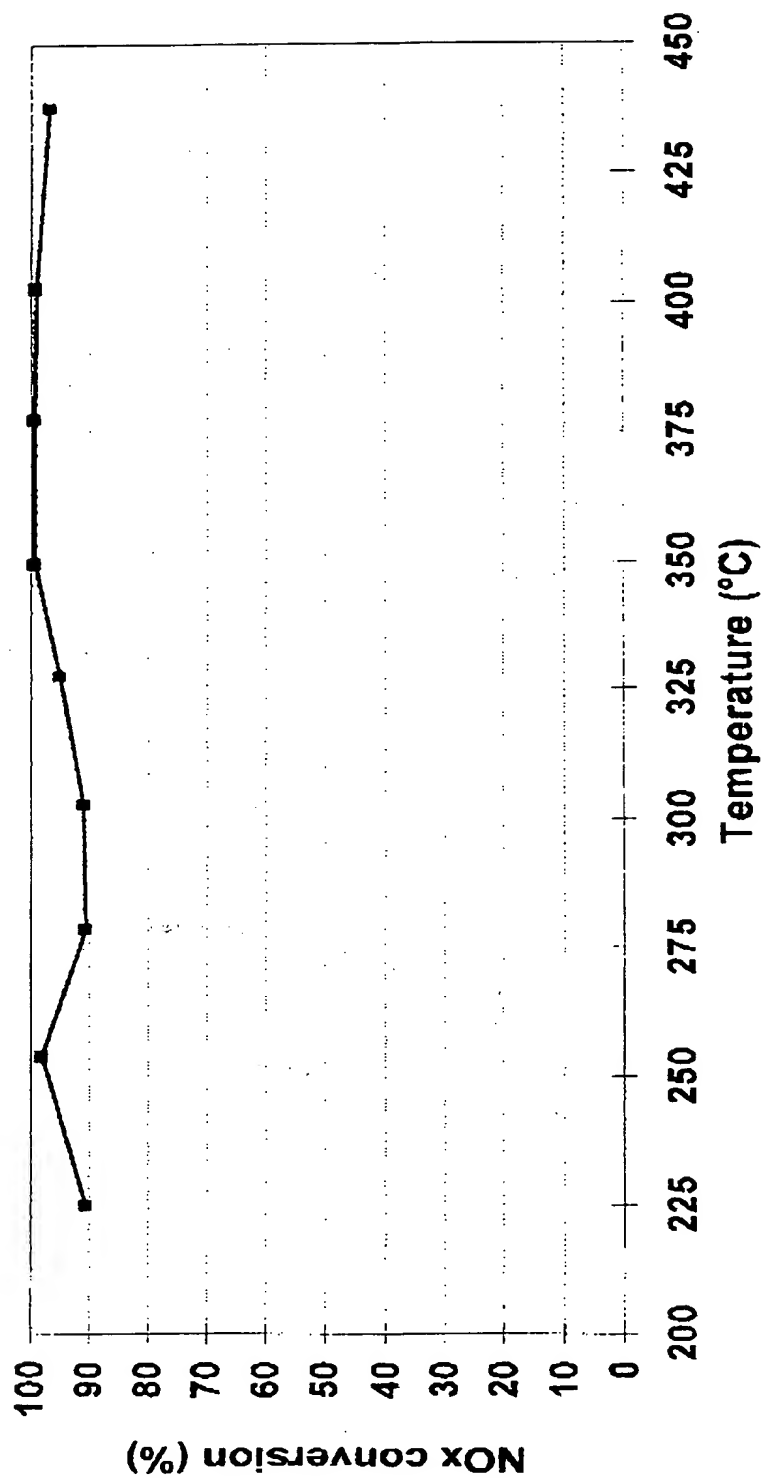
# Oxi-cat + SCR-cat



**THIS PAGE BLANK (USPTO)**

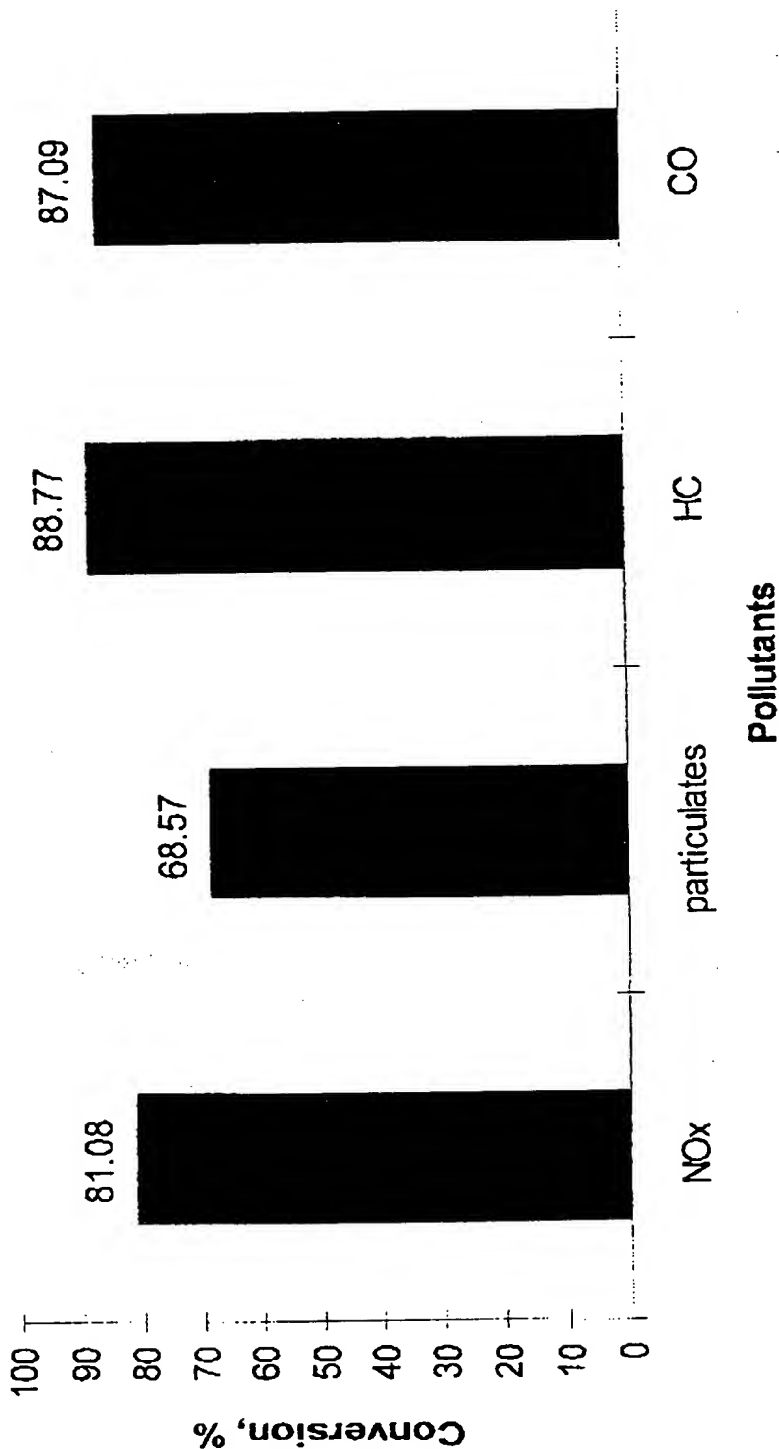
3/4

**NOx conversion over Vanadium based SCRT catalyst system**  
**100% NH3 injection, (SV: 40000 - 70000)**



**THIS PAGE BLANK (USPTO)**

# R49 Test Results: SCRT-System 80% NH3 injection



PCT/GB99/00292

Johnson Matthey

27/1/99

**THIS PAGE BLANK (USPTO)**